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# Mass transfer in annular electrolytic cells with gas stirring

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Mass transfer towards the inner electrode and the wall electrode was studied in an annular cell stirred with an inert gas bubble flow. Experimental data obtained for the wall electrode follow the relationship found previously for circular cells; namely

$$Sh = 0.231(Sc\,Ga)^{1/3}(L/D_e)^{-0.194}\varepsilon^{0.246}$$

Study of the influence of gas hold-up on the mass transfer rate towards the inner wall electrode has yielded the following relationship:

$$Sh_\infty = 0.315(Sc\,Ga)^{1/3}\varepsilon^{0.231}$$

**Nomenclature**

| | |
|---|---|
| $A$ | electrode surface ($cm^2$) |
| $a$ | factor in Equation 5 |
| $b$ | exponent in Equation 5 |
| $C_0$ | electrolyte concentration ($mol\,cm^{-3}$) |
| $D$ | diffusivity ($cm^2\,s^{-1}$) |
| $D_c$ | column diameter (cm) |
| $D_e$ | equivalent diameter of annulus (cm) |
| $F$ | Faraday's constant |
| $g$ | acceleration due to gravity ($cm\,s^{-2}$) |
| $Ga$ | Galileo number $= L^3gv^{-2}$ |
| $I$ | limiting current (A) |
| $K, K_x, K_\infty$ | mass transfer coefficients ($cm\,s^{-1}$) |
| $L$ | electrode length (cm) |
| $Sc$ | Schmidt number $= D^{-1}$ |
| $Sh, Sh_\infty$ | Sherwood number, $Sh = KLd^{-1}$, $Sh_\infty = K_\infty LD^{-1}$ |
| $V_s$ | gas superficial velocity ($cm\,s^{-1}$) |
| $x$ | position along the electrode (cm) |
| $z$ | position along the column (cm) |
| $Z$ | number of electrons interchanged in the electrochemical reaction |
| $\varepsilon, E$ | gas hold-up |
| $v$ | kinetmatic viscosity |

## 1. Introduction

The stirring produced by the rise of the gas bubbles in electrolytic cells enhances the mass transfer towards the electrodes. The gas can be generated at the electrodes (gas evolving electrodes) or introduced from the outside. Recent work [1–3] has shown that gas hold-up is a useful variable for the interpretation of mass transfer in cells with gas stirring. Cavotorta and Böhm [1] found that for circular cells the following correlations were valid:

$$Sh = 0.231(Sc\,Ga)^{1/3}(L/D_e)^{-0.194}\varepsilon^{0.246} \quad (1)$$

$$Sh_\infty = 0.256(Sc\,Ga)^{1/3}\varepsilon^{0.254} \quad (2)$$

Equation 1 holds for short mass transfer lengths and Equation 2 for fully developed mass transfer.

Piovano *et al.* [4] measured mass transfer rates at planar electrodes and expanded metal electrodes placed in the centre of a circular bubble column. For planar electrodes they found the relationship:

$$Sh = 0.362(Sc\,Ga)^{1/3}\varepsilon^{0.235} \quad (3)$$

From these relationships it can be deduced that the mass transfer coefficient for the electrode placed in the centre of the cell is 45–50% greater than for the wall electrode, in agreement with the radial variation of the gas hold-up, and the variation of the radial component of the liquid circulation velocity [5, 6].

In this work mass transfer coefficients were determined experimentally in annular cells where gas is introduced through the bottom of the column. The effect of the stirring produced by the gas on mass transfer towards an inner wall electrode and an outer wall electrode was studied.

## 2. Experimental details

The experimental set-up is shown schematically in Fig. 1. The cell was a circular column constructed from a lucite tube, 5 cm inner diameter and 130 cm high. The gas (nitrogen) was introduced through perforated lucite plates (Table 1) placed at the bottom of the column. The experiments were carried out with no net liquid circulation.



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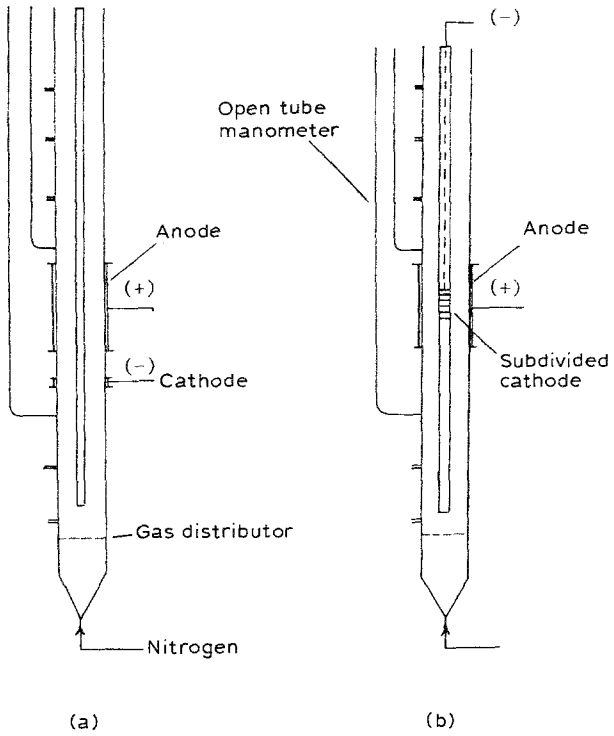


Fig. 1. Experimental set-up: (a) annular cell with electrode on the outer wall; (b) annular cell with electrode on the inner wall.

When studying the mass transfer towards the outer wall electrode (Fig. 1a) three inert tubes of different diameters were used to form the inner wall in order to vary the dimensions of the annulus ($d_1$ = 0.8 cm, $d_2$ = 1.5 cm and $d_3$ = 2.5 cm). The working electrode was 5.0 mm in length.

When studying the mass transfer towards the inner tube a 1.62 cm diameter cylinder was used, (Fig. 1b), having an electrode divided in five segments. The electric circuit was designed so that it was possible to measure the current circulating through each cathode working alone, through each cathode all being connected, and for successively longer cathodes obtained by coupling two or more neighbouring electrodes together. This allowed the determination of global mass transfer coefficients, and also of local coefficients for different positions when all the segments were working.

Table 2 presents the lengths of the five segments and the investigated lengths, obtained by combination of the same.

The working electrodes were placed in the zone of constant gas hold-up, that is 30 cm from the gas distributor. (Fig. 2 shows the gas hold-up distribution as a function of the position along the column for some of the gas velocities studied).

All the working electrodes (cathodes) were constructed in pure nickel; the anode was a nickel-plated copper tube, 14 cm high, forming part of the column wall.

*Table 1. Gas distributor characteristics*

| *Gas distributors* | *Number of orifices* | *Hole diameter (mm)* |
|---|---|---|
| D1-1 | 1 | 1 |
| D1/2-6 | 6 | 0.5 |

*Table 2. Subdivided electrode*

| *Segment (mm)* | *Investigated lengths (mm)* |
|---|---|
| 2.8 | 2.8 |
| | 6.6 |
| 6.6 | 9.3 |
| | 9.4 |
| 9.3 | 10.1 |
| | 11.2 |
| 10.1 | 18.7 |
| | 28.8 |
| 11.2 | 40.0 |

The mass transfer coefficients were determined using the limiting current technique:

$$k = I/AZFC_0 \qquad (4)$$

As a test reaction the reduction of ferricyanide ions in alkaline media was used. The electrolytic solution employed was 0.01 equimolar in potassium ferro- and ferricyanide; 0.5 M sodium hydroxide was added as inert electrolyte.

The gas hold-up was determined by the manometric method. Nitrogen, humidified before entering the cell, was used as sparging gas; the flow rate was measured with rotameters (for more experimental details, see [1]).

## 3. Results and discussion

### 3.1. *Mass transfer towards the outer wall electrode*

The introduction of solid lucite cylinders of different diameters coaxial to the external wall allowed the study of annular cells with different equivalent diameters ($D_e$). Figure 3 shows typical experimental results obtained with these cells. The correlation obtained in previous work with circular cells (Equation 1) is also included.

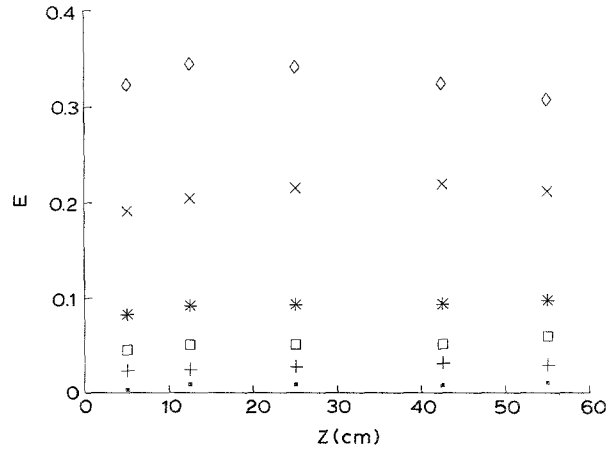


Fig. 2. Axial gas hold-up distribution in the annular column. Distributor D1-1. Gas superficial velocity, $V_s$: (●) 0.19, (+) 0.56, (*) 1.12, (□) 1.94, (×) 3.67, and (◇) 5.47 cm s$^{-1}$.

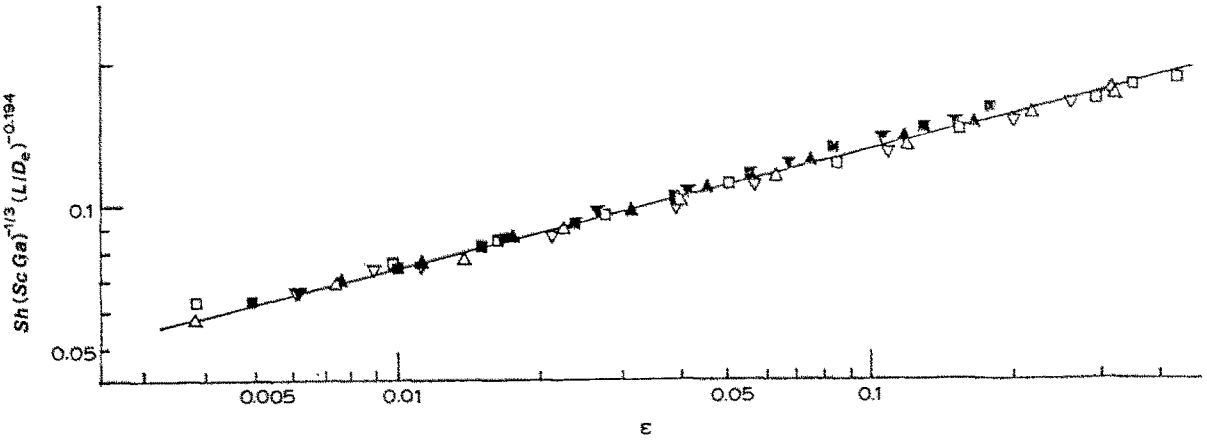


Fig. 3. Mass transfer to the outer wall electrode in different annular cells (general correlation). For D1/2-6: $d_1$ (□), $d_2$ (△) and $d_3$ (▽). For D1-1; $d_1$ (■), $d_2$ (▲) and $d_3$ (▼).

If the column diameter is replaced by the equivalent diameter of the annulus in Equation 1, it can be seen that this correlation is also valid for annular cells with equivalent diameter $> 2.5$ cm. However, it must be pointed out that at a given gas flow rate, in the annular column the velocity of the gas will be greater than in the tube without concentric cylinder, and will increase as the diameter of the inner cylinder increases. On the other hand, gas hold-up becomes higher as the gas velocity increases. So, the gas hold-up will be greater as the diameter of the inner tube increases, and the same happens with the mass transfer coefficient.

For instance, with the introduction of a 2.5 cm diameter cylinder in a 5 cm diameter cell, the superficial gas velocity rises by 33%, the gas hold-up by 45% and, consequently, the mass transfer coefficient increases by 10%.

### 3.2. *Mass transfer coefficients towards the inner electrode*

Figure 4 shows local coefficients ($k_x$) obtained with a 40 mm long electrode for superficial gas velocities varying between 0.19 and 3.67 cm s$^{-1}$. As can be seen

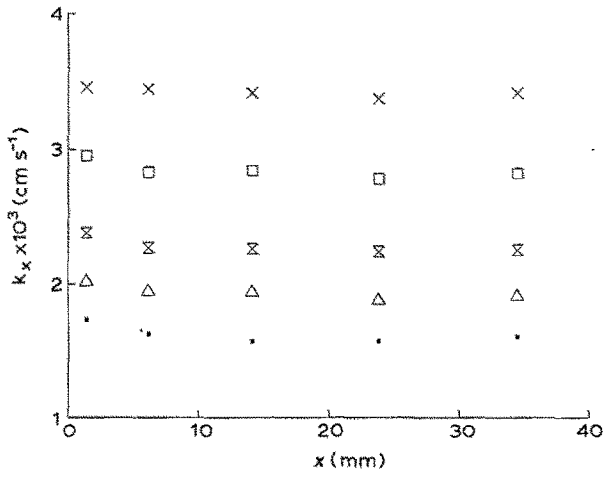


Fig. 4. Mass transfer to the inner wall-electrode of an annulus: local mass transfer coefficients. Gas superficial velocity, $V_s$: (●) 0.19, (△) 0.38, (⧖) 0.84, (□) 1.94 and (×) 3.67.

there is a small effect of the position at the leading edge of the electrode system.

Figure 5 presents the effect of the superficial gas velocity ($V_s$) on the global mass transfer coefficients ($k$) obtained for a 11.2 mm long electrode which is part of the inner cylinder of the annular cell. In the same figure the influence of the gas velocity on the gas hold-up in the electrode zone ($\varepsilon$) is represented for the same annular cell. Both variables have the same functional relationship with $V_s$. As proposed by Cavatorta and Böhm [1] it is better to use gas hold-up as a fluid dynamic variable in order to eliminate the influence of the gas distributor employed. Therefore typical values of $k$ for some of the electrodes studied are presented in Fig. 6 as a function of the gas hold-up.

The figure shows that the relationship between $k$ and $\varepsilon$ has the form

$$k = a\varepsilon^b \tag{5}$$

which is in agreement with results obtained with other bubble stirred systems.

Also in Fig. 6 it can be seen that for the smaller electrodes the global transfer coefficients are slightly higher. Figure 7, representing coefficients $k$ against electrode length for some gas hold-ups, also indicates a small dependence between $k$ and $L$ for lengths smaller than 10 mm. For these small mass transfer lengths a dependence of $Sh$ with $(L/D)^{-0.054}$ was found, which is of little significance. In consequence, all the experimental data (for small and big transfer lengths) were correlated eliminating the variable $(L/D)$. The following relationship was obtained:

$$Sh = 0.314(Sc\,Ga)^{1/3}\varepsilon^{0.221} \tag{6}$$

with a standard deviation of 3.7%.

Using the local coefficients of the zone of constant $k$ (Fig. 4) in order to obtain the correlation for fully developed mass transfer, the following equation results:

$$Sh_\infty = 0.315(Sc\,Ga)^{1/3}\varepsilon^{0.231} \tag{7}$$

with a standard deviation of 2%.

The similarity of Equations 6 and 7 is due to the small effect of length on the mass transfer rate.

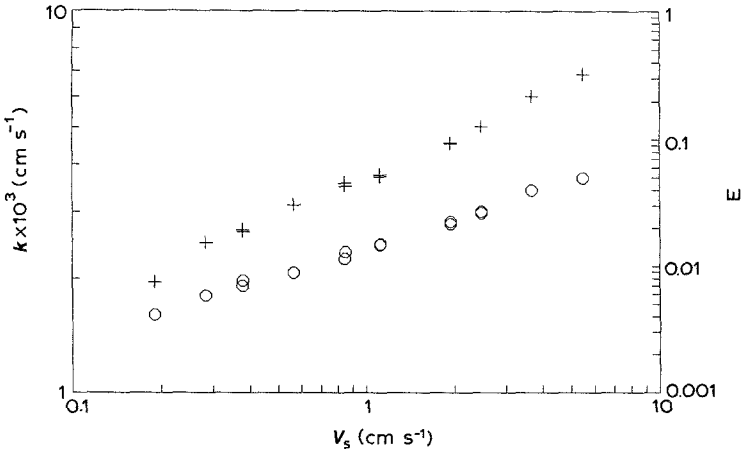


Fig. 5. Effect of superficial gas velocity on the mass transfer coefficient and the gas hold-up (inner wall electrode). (○) $k$ (cm s$^{-1}$) and (+) $E$.

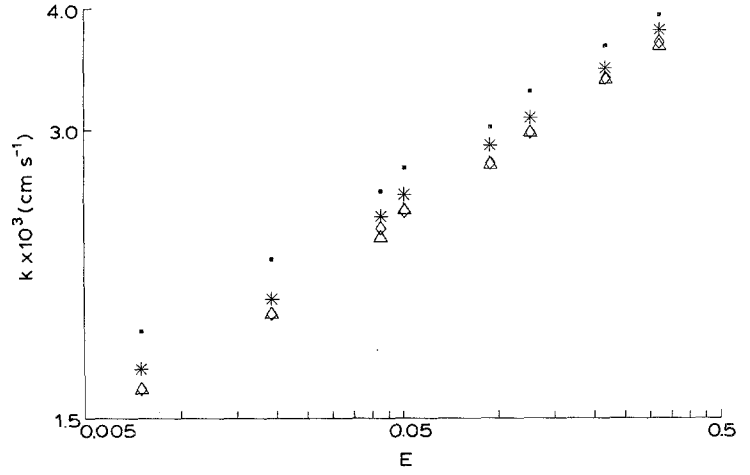


Fig. 6. Mass transfer coefficient as function of gas hold-up for inner wall electrodes of different length, *Le*: (●) 2.8 (∗) 9.4, (◇) 28.8 and (△) 40.0 mm.

## 4. Concluding remarks

(i) Mass transfer data in annular and in circular electrolytic cells correlate with the same functionality.

(ii) Transfer towards the outer wall of an annulus follows the correlation obtained for circular cells using equivalent diameter instead of column diameter.

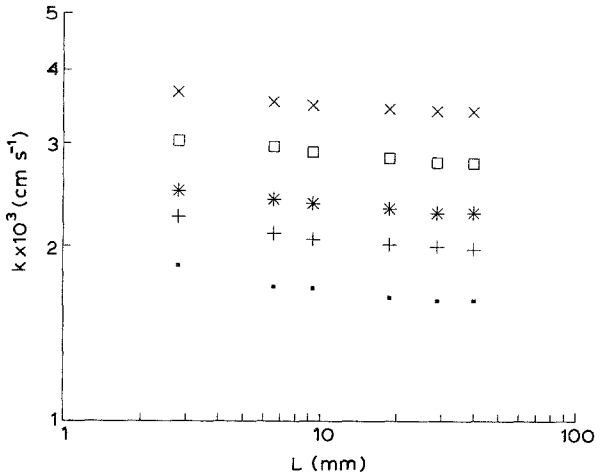


Fig. 7. Variation of global mass transfer coefficients with electrode length. (Inner wall electrode.) $E$: (●) 0.0075, (+) 0.0187, (∗) 0.0453, (□) 0.0947 and (×) 0.2187.

(iii) Transfer towards the inner cylinder shows a smaller effect of transfer length than for circular cells. For design purposes Correlation 7 can be used in order to evaluate global mass transfer coefficients independently of transfer length.

(iv) Economically, annular cells (with outer wall or inner wall electrodes) are more convenient because with a given volumetric gas flow rate the transfer coefficients obtained are higher than for circular cells.

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